Supporting Information

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**PVD**

Thin films of Cu were prepared inside a Temescal BJD-1800 chamber, refurbished by Technical Engineering Services, which is equipped with two electron (e)-guns and a thermal source for simultaneous evaporation of up to three materials. The deposition rate and thickness were accurately monitored by a quartz crystal microbalance. A dicing saw was used to cut 4-inch Al₂O₃ and Si wafers into 27 mm × 42 mm (large-format) substrates. All samples were sonicated first in a 60:30:10 mixture of acetone: isopropanol:water, next in Millipore water, and subsequently dried with a N₂ gun. For Al₂O₃(0001), four substrates were distributed onto a 4-inch Si test wafer and subsequently pumped down within the chamber. After pump down, the stage was stabilized at a temperature of 100 °C and a 5-nm layer of Ti was first deposited on Al₂O₃(0001) to increase the adhesion of Cu to the substrate. After the Ti deposition, 500 nm of Cu was deposited at 2 Å/s without breaking vacuum to ensure a clean interface between Cu and Ti. For Si(100), (111), and (110), the native oxide was removed with buffered hydrofluoric acid (BHF) before loading the samples within the chamber. Previous studies show that a BHF treatment not only removes the native oxide but also hydrogen terminates the Si surface, facilitating a clean interface for Cu growth (13, 21). After pumping down the chamber, 100 nm of Cu was deposited at 2 Å/s on the Si(100) and (111) substrates.

**XRD**

Multiple XRD techniques were used to characterize the texture of the Cu thin films (PANalytical XPert diffractometer, Cu-Kα radiation of 1.541874 Å). Symmetrical 20–2θ scans were performed to determine the out-of-plane texture of the Cu thin films, whereas pole figure analysis was performed to determine both the out-of-plane and in-plane texture and the epitaxial relationship between the Cu films and substrates. For the pole figure measurements, a flat graphite monochromator on a diffracted beam site was used to reduce the effect of sample fluorescence. The diffraction angle (2θ) was set to the Bragg angle relevant to each Cu thin-film sample while the sample rotation (φ) and tilt (χ) were scanned between 0–360° and 0–90°, respectively. The Bragg angle was set to Cu(200) for Cu/Ti/Al₂O₃(0001), Cu(111) for Cu/Si(100), and three pole figure measurements were performed on Cu/Si(111) with Bragg angles set to Cu(200), (111), and (220). The three pole figure scans were used to construct an orientation distribution function for Cu/Si (111) and subsequently calculate the inverse pole figure.

**ECSTM**

ECSTM images were obtained using a Nanoscope E microscope (Digital Instruments, Veeco) equipped with a built-in three-electrode potentiostat. The experimental procedures were as described in detail elsewhere (24).

The STM electrochemical cell, custom-crafted from Kel-F (Emco Industrial Plastics, Inc.), was fitted with a Pt counter electrode and a miniature leakless Ag/AgCl (3.4 M KCl) reference electrode (Innovative Instruments, Inc.). The STM tips were prepared by an electrochemical etch of a 0.25-mm-diameter tungsten wire (Sigma-Aldrich) in 1.0 M KOH at 15 V_ac.

For the ECSTM experiments, smaller samples (0.9 cm × 0.9 cm) of the Si(100)-supported Cu films were pared from the larger specimens and used without pretreatment. The sample was immersed in 0.1 M HClO₄ (Sigma-Aldrich) and, from the open-circuit potential, was scanned at 50 mV s⁻¹ to −0.76 V vs. RHE to reduce any surface cuprous oxide back to Cu metal. The latter was then held at −0.24 V vs. RHE, the potential at which the ECSTM scans were acquired. For large-area (greater than 10 mm × 10 mm) scans, E_max = 250 mV and I_ref = 2 nA; the tunneling current was increased to 20 nA for atomic-resolution images. All solutions were prepared with 18.2 MΩ-cm Nanopure water (Thermo Fisher Scientific).

**Electrochemistry and Product Detection**

Electrochemical experiments were performed in a custom compression cell described in a previous report (7). Elastomer foams (Viton fluoroelastomer foam) were used as a backing for the working electrode to prevent cracking of the samples. An anion exchange membrane (Selemon AMV, AGC Inc.) was used to separate the working- and counter-electrode compartments, which were both filled with 10 mL of 0.1 M KHCO₃ (Sigma-Aldrich, 99.99% metals basis). CO₂ (5.0 N, Praxair) was bubbled through the cell at a flow rate of 20 sccm using a mass-flow controller (MKS Instruments). The pH of the CO₂-saturated KHCO₃ electrolyte equilibrated at 6.8 (accurate basic AB15 pH meter and accuTupH pH electrode, Fisher Scientific). Electrochemical data were collected using a three-electrode configuration (Ag/AgCl reference, Accumet) with a Bio-Lock VMP3 potentiostat capable of electrochemical impedance spectroscopy (EIS). Potentiostatic EIS measurements were performed to identify the frequency that allowed for an accurate measurement of the uncompensated solution resistance (R_solution) of the cell. For all electrochemical measurements, 85% of R_solution was compensated by the potentiostat and the remaining 15% was manually postcorrected in an identical fashion to that described in our previous work (7).

One-hour CA experiments were performed at four different potentials to characterize the activity and selectivity of the Cu thin films for the electrochemical reduction of CO₂. Gas-phase products were measured four times over the hour-long CA by connecting a gas chromatograph (SRI Instruments 8610C with HayeSep D and MS13X columns) on-line. Liquid-phase products were collected after each 1-h electrolysirun and quantified using NMR spectroscopy with water suppression (Varian Inova 600-MHz NMR spectrometer).
Symmetrical XRD scans, $\phi$-scans, and rocking curves ($\omega$-scans) for Cu thin films grown (A) directly on Al$_2$O$_3$(0001) and (B) with a Ti binding layer. Symmetrical scans reveal the presence of only the Cu(111) peak indicating that the Ti binding layer does not influence the out-of-plane texture. A comparison of the $\phi$-angles between the Al$_2$O$_3$(204) and Cu(200) peaks shows that the in-plane texture is equivalent for both samples. Rocking curve scans show similar values for the FWHM, demonstrating that the Cu thin films are similar in quality.

X-ray pole figure scans for Cu grown on Si(111) showing the (A) Cu(111), (B) Cu(200), and (C) Cu(022) Bragg reflections.

Atomic model showing the low Miller index facets (111), (110), and (100) exposed on a Cu(751) surface. The Cu(751) surface can be described by the microfacet notation Cu $S$-[111] + 4(110) + 2(100)].
Fig. S4. A Cu(200) X-ray pole figure for Cu on Si(110) shows identical thin-film texture to Cu on Al₂O₃(0001).

Fig. S5. Large-scale ECSTM images of Cu on (A) Si(110), (B) Si(100), and (C) Si(111).
Total current densities and current efficiencies from electrochemical CO$_2$R on Cu(111), (100), and (751) at four different potentials. The values are percentages unless otherwise noted. SEs are indicated for all gas-phase products.
Fig. S7. Total CO$_2$ reduction rates as a function of potential for polycrystalline Ag, polycrystalline Cu (poly Cu), Cu(100), (111), and (751). In contrast to Ag, mass transport limitation of CO$_2$ is not observed for any of the Cu electrodes.

Fig. S8. Partial current densities for $>$2e$^-$ C1, C2, and C3 products as a function of potential for Cu(111), (751), and (100). The increase in partial current densities for C2 and C3 products indicates that Cu(751) and (100) are more active for C–C coupling than Cu(111).

Fig. S9. Current efficiencies for $>$2e$^-$ hydrocarbon and oxygenate products as a function of potential for Cu(111), (751), and (100). All surfaces are more selective for hydrocarbons than oxygenates across the measured range of potentials.
Fig. S10. Partial current densities for $\geq 2e^-$ hydrocarbon and oxygenate products as a function of potential for Cu(111), (751), and (100). At $\sim -0.89$ V vs. RHE, Cu(751) shows the highest partial current density for oxygenates indicating that stepped surfaces have greater activity for oxygenates.